AFRL-RZ-WP-TP-2012-0127

MINUTE DOPING WITH DELETERIOUS RARE EARTHS IN $YBa_2Cu_3O_{7-\delta}$ FILMS FOR FLUX PINNING ENHANCEMENTS (POSTPRINT)

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FEBRUARY 2012

AIR FORCE RESEARCH LABORATORY
PROPULSION DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7251
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
February 2012	Journal Article Postprint	01 January 2004 – 01 January 2006

4. TITLE AND SUBTITLE

MINUTE DOPING WITH DELETERIOUS RARE EARTHS IN $YBa_2Cu_3O_{7-\delta}$ FILMS FOR FLUX PINNING ENHANCEMENTS (POSTPRINT)

5a. CONTRACT NUMBER
In-house

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62203F

6. AUTHOR(S)

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5d. PROJECT NUMBER
3145

5e. TASK NUMBER
32

5f. WORK UNIT NUMBER
314532ZE

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Mechanical Energy Conversion Branch (AFRL/RZPG)
Energy/Power/Thermal Division
Air Force Research Laboratory, Propulsion Directorate
Wright-Patterson Air Force Base, OH 45433-7251
Air Force Materiel Command, United States Air Force

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Dayton, OH 45469-1390

College of NanoScale Science and Engineering
Albany, NY 12203

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL-RZ-WP-TP-2012-0127

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory
Propulsion Directorate
Wright-Patterson Air Force Base, OH 45433-7251
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/RZPG

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RZ-WP-TP-2012-0127

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

Journal article published *Applied Physics Letters*, Vol. 89, 2006.

 PA Case Number: AFRL/WS 06-0610; Clearance Date: 06 Dec 2006.

Work on this effort was completed in 2006. This paper contains color.

14. ABSTRACT

To enhance the critical current density of $YBa_2Cu_3O_{7-\delta}$ films, flux pinning centers are intentionally added to inhibit flux flow in applied magnetic fields. Here we provide an initial demonstration that the incorporation of very minor additions 1% of Y as opposed to the 10%–40% in standard substitutions of typically deleterious rare earths into high quality $YBa_2Cu_3O_{7-\delta}$ thin films provides significant improvement of the film's in-field current density. This is accomplished without reoptimization of the deposition parameters. Instead of site substitution for Y as might be expected, the deleterious rare earths potentially result in the formation of nanoparticulates.

15. SUBJECT TERMS

critical current, flux pinning, incorporation, substitutions, deleterious, rare earths, parameters, magnetic fields, flux flow

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Timothy J. Haugan
Unclassified	Unclassified	Unclassified	SAR	10	19b. TELEPHONE NUMBER *(Include Area Code)* N/A

APPLIED PHYSICS LETTERS **89**, 012503 (2006)

Minute doping with deleterious rare earths in $YBa_2Cu_3O_{7-\delta}$ films for flux pinning enhancements

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(Received 15 March 2006; accepted 2 June 2006; published online 6 July 2006)

To enhance the critical current density of $YBa_2Cu_3O_{7-\delta}$ films, flux pinning centers are intentionally added to inhibit flux flow in applied magnetic fields. Here we provide an initial demonstration that the incorporation of very minor additions ($\leqslant 1\%$ of Y as opposed to the 10%–40% in standard substitutions) of typically deleterious rare earths into high quality $YBa_2Cu_3O_{7-\delta}$ thin films provides significant improvement of the film's in-field current density. This is accomplished without reoptimization of the deposition parameters. Instead of site substitution for Y as might be expected, the deleterious rare earths potentially result in the formation of nanoparticulates. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2219391]

$YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting thin films can maintain high critical current densities (J_c) in applied magnetic fields up to a few tesla at 77 K. This property makes this material desirable for use as a high temperature superconducting (HTS) coated conductor in the form of biaxially aligned YBCO coatings on buffered metallic substrates, now over 100 m or more in length.[1–4] The in-field J_c is often attributed to the intrinsic defects of the as-grown films which act as magnetic flux pinning centers.[5] Even so, the intentional addition of alternate flux pinning centers into the YBCO films is necessary to further improve upon the in-field J_c for applications.[5–8]

In YBCO films, it is difficult to truly ascertain exactly what defects are the prominent pinning centers, since the coherence length for this high temperature superconductor is quite small, $\xi \sim 1.5-2$ nm.[5,9] Additionally, what may effectively pin in bulk material or lower quality thin films may not provide the same level of pinning in thin films of higher quality material.[10] Several reports of improved pinning in YBCO thin films have been published recently.[11–16] One effective method, initially reported by Haugan *et al.*, incorporated nanoparticulate dispersions into YBCO films.[11,12] Subsequent work by others have also demonstrated improvement with nanoparticulates or stacked nanoparticles.[13–16] Another way to improve pinning is by partial rare earth (RE) substitution for Y since YBCO and other REBCO superconductors have similar structures.[10,17] As a periodic site substitution, the replacement atom can cause strain induced improvements. This doping of yttrium sites with other rare earths (e.g., Sm, Eu, Gd, etc.) often provides modest improvements but not as high as the nanoparticulate additions.

However, certain rare earth elements have been shown to be less desirable for making REBCO films, for example, Pr, Ce, and Tb. These elements do not form or not readily form the proper REBCO phase in bulk powders.[10,18,19] When used as dopants in quantities that other REs enhance performance, typically 10% Y substitution or greater, they degrade the quality of YBCO. Even if a rare earth can readily form the proper REBCO superconducting phase, such as Nd and La, they can be poor dopants in YBCO by substituting undesirably into the Ba site, degrading the superconductor's performance. The deleterious dopants do differ: Tb does not degrade the T_c of YBCO, whereas Ce and Pr affect the T_c by lowering it substantially.[20]

Since these undesirable dopants are degrading in nature, it is reasonable to assume that when used in very small or minute quantities as $(Y_{1-x},RE_x)Ba_2Cu_3O_{7-\delta}$ where $x \leqslant 0.01$, or $\leqslant 1\%$ of Y, the proper density of defects may be established. Such small quantities will require that the inclusions are sufficiently dispersed as well. In bulk materials, a few percent of Pr doping of bulk YBCO has demonstrated some minor improvements to performance,[21] but none has been demonstrated in thin films. The work presented here provides an initial demonstration that the incorporation of very minor additions ($\leqslant 1\%$ of Y) of typically deleterious RE into high quality YBCO thin films provides significant improvement of the film's in-field current density, especially at 65–77 K, an expected operating temperature range of HTS machinery.[6–8] Furthermore, this enhancement can be achieved using these dopants in YBCO thin films processed under the same conditions as the undoped films. By avoiding individualized reoptimization, YBCO coated conductors can be readily tailored for a given magnetic field environment.

Powders were prepared for the compositions of $(Y_{1-x},RE_x)Ba_2Cu_3O_{7-\delta}$ where RE=Tb, Ce, Pr, Nd, or La and $x=0.0001$, 0.001, 0.01, and 0.1 from the precursor powders of Y_2O_3, $BaCO_3$, CuO, Tb_4O_7, CeO_2, Pr_2O_3, Nd_2O_3, and La_2O_3 (all nominally 99.99+% pure). Initial targets, with compositions RE=Tb, Ce, or Pr and $x=0.001$, 0.01, and 0.1, were made by first preparing powders with compositions $YBa_2Cu_3O_{7-\delta}$ and $(Y_{0.9},RE_{0.1})Ba_2Cu_3O_{7-\delta}$. Final compositions were made by diluting the $(Y_{0.9},RE_{0.1})Ba_2Cu_3O_{7-\delta}$ powders with the $YBa_2Cu_3O_{7-\delta}$ powder before final reaction at 940 °C. Further powders were made directly from oxides

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without diluting. The powders were dried, mixed, and calcined at 850 and 880 °C, respectively. Targets for use in pulsed laser deposition (PLD) were then manufactured and fully reacted followed by sintering at 940 °C until they reached a density of at least 80% of the theoretical density.

The various thin films of $(Y_{1-x},RE_x)Ba_2Cu_3O_{7-\delta}$ were made by PLD using the conditions previously optimized for YBCO.[12,22] The depositions were performed on single crystal strontium titanate (STO) and lanthanum aluminate (LAO) substrates. A Lambda Physik LPX 305 KrF excimer laser ($\lambda=248$ nm) was used at a repetition rate of 4 Hz and a laser fluence of ~ 3.2 J/cm^2. The background pressure in the chamber was reduced to $<6\times10^{-6}$ Torr prior to depositions. The oxygen pressure during the deposition was maintained at 300 mTorr for all targets with a gas purity of 99.999%. The deposition temperature was 775 °C. After deposition, an *in situ* oxygen anneal was performed at 500 °C for 30 min.

The critical transition temperature (T_c) and magnetic J_c measurements were made with a vibrating sample magnetometer (VSM). The T_c's of the films were determined magnetically using an ac susceptibility technique with some additional resistive measurements. Samples were subsequently acid etched at the corners, and thickness measurements were performed using a profilometer to measure the thickness of the films. The film thickness and dimensions of each sample were measured multiple times to reduce errors in determination of the superconducting volume to <5%. Film thicknesses were typically ~ 0.3 μm. Transport critical currents were also performed on some samples in addition to magnetic measurements.

The T_c's of the RE minutely doped films ranged between 89.1 and 92.7 K which are comparable to those of reference YBCO films. However, the Ce and Pr doped films showed a marked decrease in T_c as the concentration was increased, lowering to 87.1 and 86.1 K, respectively, at the 10% levels. The J_c's of the minutely doped YBCO had varying effects. See Fig. 1 for pinning force plots at 77 and 65 K, respectively. The values plotted in the figure are representative values from several depositions. Multiple depositions were made to verify repeatability of the results; in several cases additional targets were processed as well to ensure consistency. As an example, the first deposition of YBCO with minutely doped Pr (1%) showed little difference from YBCO, but subsequent depositions consistently demonstrated enhanced performance. Samples with 10% concentration of the dopants were also made for comparison. These results were consistent with previously published work regarding the degrading nature of these elements as inclusions in the YBCO structure.

Note that at 77 K, 1–5 T, the best pinning improvement among the tested dopants was accomplished with a 0.1% Nd doping of the YBCO. A study showed that Nd doping at higher levels in YBCO thin films processed at typical YBCO conditions was not effective for flux pinning enhancement in applied magnetic fields.[23] This is attributed to the Nd substitutions into Ba sites in the unit cell as opposed to the desired Y site. At 65 K, the best pinning enhancement occurred for 1% Tb doping of the YBCO. Figure 2 shows the J_c versus magnetic field performance at 65 K for Tb doping. As the doping concentration of Tb was decreased to 0.01%, its effectiveness for pinning was removed. In general, for the dopants studied, replacing Y with about 0.1% dopant tended to improve the in-field properties of the resulting YBCO across

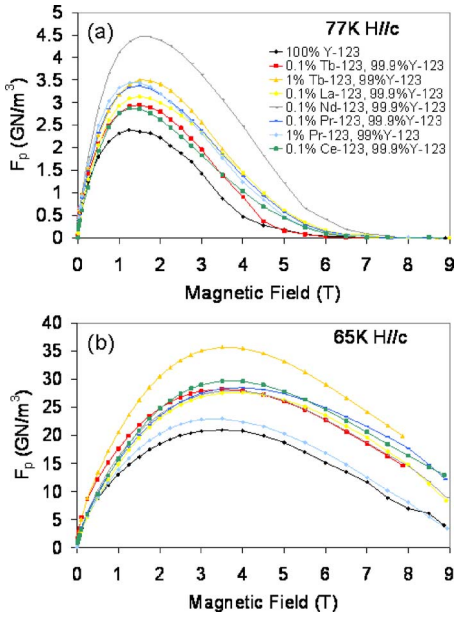

FIG. 1. (Color online) Pinning force plots for the minutely doped $(Y_{1-x},RE_x)Ba_2Cu_3O_{7-\delta}$ films ($x=0.01$ and 0.001). YBCO is the solid black line. An $x=0.1$ Tb doped YBCO is included for comparison which performed the best of the $x=0.1$ level doping (10% of Y). The pinning force was calculated by $F_p=J_cB$: (A) at 77 K and (B) at 65 K.

both temperature regimes with the exception of 1% Tb. Since the temperature dependences of the minutely doped YBCO films are dissimilar for certain dopants, the reason the dopants act as pinning centers may differ.

Analysis of the elemental composition by secondary ion mass spectroscopy (SIMS) of the samples indicates the presence of the dopants throughout the sample. See Fig. 3 for the depth profile of the compositional analyses. Although mixed in such small quantities and processed multiple times, the minute dopants are indeed present throughout the films. However, the SIMS data do not clarify the dispersion on the smaller nanoscopic level to determine if there is site substitution or not. Note in Fig. 3 that the fairly level ^{63}Cu count is due to mass interference with ^{47}Ti^{16}O. The angular dependence of J_c with respect to the applied magnetic field of the Tb samples also shows no extraneous peaking than the established YBCO form, indicating no preferred pinning orientation.

A question that remains is whether the minute dopants are site substituting with the Y or causing secondary phase precipitates. Figure 4 shows a high resolution scanning elec-

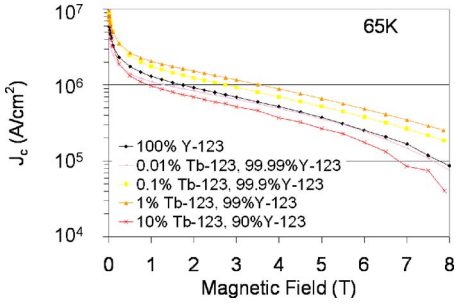

FIG. 2. (Color online) J_c is plotted as a function of magnetic field for the $(Y_{1-x},Tb_x)Ba_2Cu_3O_{7-\delta}$ films ($x=0.1$, 0.01, 0.001, and 0.0001). The 10%, 1%, and 0.1% doping of Y are representative data. The 0.01% doping is a single deposition. The data are for magnetic J_c.

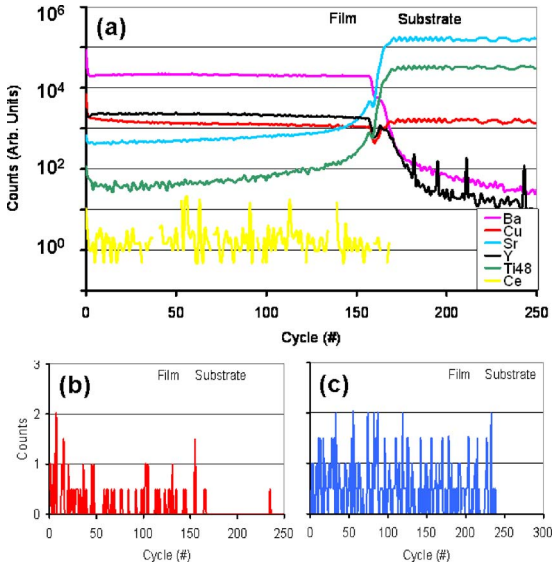

FIG. 3. (Color online) Examples of SIMS data for the minutely doped films showing the presence of the minor dopants in the $(Y_{1-x},RE_x)Ba_2Cu_3O_{7-\delta}$ films: (A) Overall data for RE=Ce, $x=0.01$; (B) close-up for RE=Tb, $x=0.01$; and (C) close-up for RE=Pr, $x=0.001$. The Cu concentration in the figure appears to be constant beyond the interface. It should be noted that it is an artifact due to the mass interference between ^{63}Cu and $^{47}Ti^{16}O$ in the STO substrate. Note that the kink in the signal near the interface is an artifact, since the sputtering yield and ionization probability change at the interface.

tron micrograph (SEM) of a Nd doped YBCO film as an example. Here, as with the other films, nanoparticles are seen on the surface, suggesting the formation of nanoparticulates by the dopants. Although nanoparticles such as these are sometimes seen in plain YBCO films, the density of the nanoparticulates is significantly higher and more dispersed in the doped films. This is consistent with the relative effectiveness of site substituting standard RE dopants at higher percentages versus nanoparticulate pinning.

YBCO was doped with minute amounts ($\leqslant 1\%$ of Y) of typically degrading rare earths and thin films made by pulsed laser deposition. Results demonstrate that minute doping of YBCO with these rare earths can improve J_c of the sample by over 200% at a few tesla. Tb and Nd seem to be the best dopants of those presently attempted at 65 and 77 K, respectively. In every case, the same deposition parameters were used as that for pure YBCO with no need for reoptimization of the films.

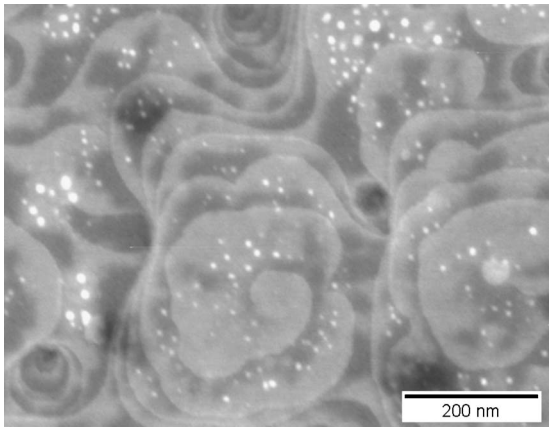

FIG. 4. (Color online) SEM of the surface for an $(Y_{0.999}Nd_{0.001})Ba_2Cu_3O_{7-\delta}$ film showing the formation of nanoprecipitates. The nanoparticulates were seen in several of the films examined, indicating that as opposed to Y-site substitution, nanoparticles are formed.

The Air Force Office of Scientific Research and the Propulsion Directorate of the Air Force Research Laboratory supported this work. The authors thank I. Maartense for performing the ac susceptibility measurements and N. Pierce for the SEM.

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